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TITLE: COMPARISON OF PREDICTED AND MEASURED PULSED-COLUMN
PROFILES AND INVENTORIES

AUTHOR(S): C. A. Ostenak and A. F. Cermak

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

COMPARISON OF PREDICTED AND MEASURED PULSED-COLUMN PROFILES AND INVENTORIES

C. A. OSTENAK
Los Alamos National Laboratory
Los Alamos, New Mexico 87545, USA
(505) 667-3382

A. F. CERMAK*
General Electric Company
Wilmington, North Carolina 28402, USA
(919) 343-6664

ABSTRACT

Nuclear materials accounting and process control in fuels reprocessing plants can be improved by near-real-time estimation of the in-process inventory in solvent-extraction contactors. Experimental studies were conducted on pilot- and plant-scale pulsed columns by Allied-General Nuclear Services (AGNS), and the extensive uranium concentration-profile and inventory data were analyzed by Los Alamos and AGNS to develop and evaluate different predictive inventory techniques. Preliminary comparisons of predicted and measured pulsed-column profiles and inventories show promise for using these predictive techniques to improve nuclear materials accounting and process control in fuels reprocessing plants.

I. INTRODUCTION

A. Background

Reprocessing plants commonly use the Purex solvent-extraction process for the separation and purification of uranium and plutonium from spent nuclear fuels. Three types of solvent-extraction contactors that typically are employed in this process are mixer-settlers, pulsed columns, and centrifugal contactors. For equal process throughput, mixer-settlers and pulsed columns generally contain a substantially larger inventory of nuclear materials than do centrifugal contactors.

Safeguards studies¹⁻⁶ show that estimating contactor inventory to 5-10% or better will provide acceptable sensitivity to detect short-term losses of nuclear materials in reprocessing plants. (Over longer accounting periods, column-inventory uncertainty has a smaller effect as throughput-measurement errors accumulate.) Therefore, both nondestructive assay techniques

and predictive techniques based on computerized chemical models, empirical algorithms, and process monitoring instrumentation are being developed and evaluated for contactor inventory estimation.⁷⁻¹⁰

B. Current Study

Pilot- and plant-scale pulsed-column studies were sponsored by the Los Alamos National Laboratory at the Allied-General Nuclear Services (AGNS) facilities at Barnwell, South Carolina. The pilot-scale study,⁹ comprising 15 mass-transfer tests using unirradiated natural uranium as the solute, was designed to investigate pulsed-column concentration profiles and inventories for various steady-state operating conditions. Both extraction/scrub and stripping pulsed columns were used to simulate runs in the first uranium-plutonium cycle, second uranium cycle, and second and third plutonium cycles under coprocessing Purex conditions. In all pilot-scale runs, samples were taken from along each steady-state pulsed column to estimate the uranium concentration profiles. Also, a few columns were drained and analyzed for uranium to assess different methods for estimating pulsed-column inventory. Similarly, several plant-scale pulsed columns were drained and analyzed for uranium inventory in connection with the 1980-81 miniruns¹⁰ performed in the second and third plutonium cycles of the AGNS Barnwell facility.

In the following sections, details and results of the pilot-scale experimental study are presented along with preliminary results from the plant-scale miniruns.

II. PILOT-SCALE EXPERIMENTAL EQUIPMENT, PROCEDURES, AND CONCENTRATION PROFILES

A. Equipment

The pilot-scale experimental equipment consisted of the three glass pulsed columns (1A,

*Work performed while employed by Allied-General Nuclear Services, Barnwell, SC 29812, USA.

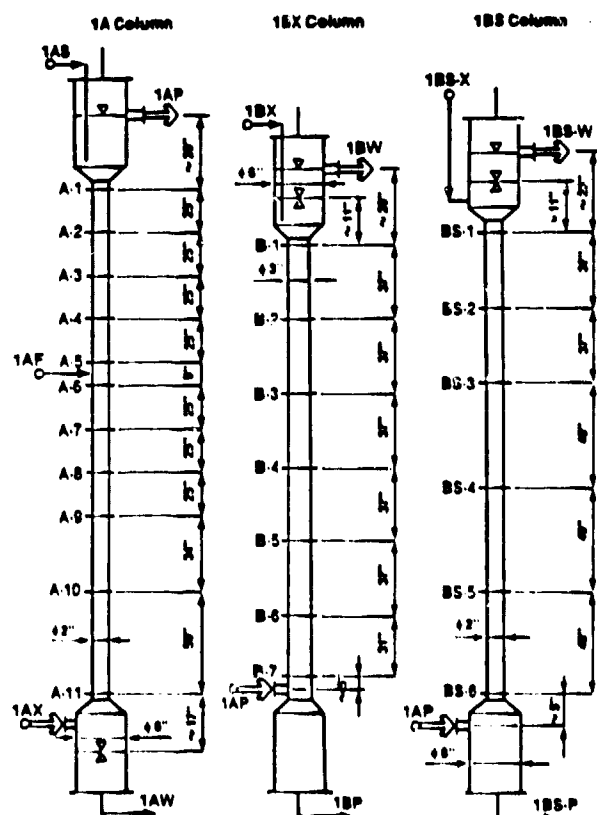


Fig. 1. Sampler locations along the 1A, 1BX, and 1BS pilot-scale pulsed columns. (Adapted from Ref. 9.)

1BS, and 1BX) shown in Fig. 1 and auxiliary equipment including pumps and stainless-steel feed, product, and waste tanks. The 2-in.- (50-mm)-diameter 1A extraction/scrub pulsed column (used for runs HS-1 through HS-6, 2D-1 through 2D-3, 2A-1 through 2A-3, and 3A-1 through 3A-3) was 26.5 ft (8.15 m) high, with a lower working (extraction) section of 13 ft (3.96 m) and an upper (scrubbing) section of 9.3 ft (2.8 m). The 3-in.- (75-mm)-diameter 1BX stripping pulsed column (used for runs HS-1 through HS-6, 2D-1 through 2D-3, and 2A-1 through 2A-3) was 22 ft (6.71 m) high, with a working section of 17 ft (5.20 m). The 2-in.- (50-mm)-diameter 1BS stripping pulsed column (used for runs 3A-1 through 3A-3) was 23 ft (7.02 m) high, with a working section of 18 ft (5.49 m).

All three pulsed columns had stainless-steel nozzle plates with 23% free surface area, 1/8-in. (3.2-mm) plate orifice diameter, and

1/16-in. (1.6-mm) plate thickness. The plates were spaced at 2-in. (50-mm) intervals along a central, 1/4-in.- (6-mm)-diameter stainless-steel tie rod.

Each pulsed column also had a 6-in.- (150-mm)-diameter top and bottom disengaging section made of glass. The top disengaging section was vented, and the bottom disengaging section was connected to a bellows-type pulser. The aqueous/organic interface was controlled automatically in the bottom disengaging section of the 1A pulsed column and in the top disengaging section of the 1BS and 1BX pulsed columns. Control of the interface was accomplished using two titanium conductivity probes to regulate an air-operated, stainless-steel control valve at the aqueous-phase outlet line.

All three pulsed columns were provided with several uranium concentration samplers. The 1A pulsed column had 11 samplers along its working section (5 for the scrubbing section and 6 for the extraction section). The 1BS and 1BX pulsed columns had 6 and 7 samplers, respectively. Sampler locations for all three columns and distances between adjacent samplers are shown in Fig. 1. Aqueous and organic samplers were each made of stainless-steel tubing having an inside diameter of 1/8 in. (3 mm). The organic sampler included a tubular end piece made of teflon.

The feed preparation tank consisted of a 500-gal. stainless-steel vessel equipped with a mechanical agitator, cooling-heating jacket, sight glass, and temperature and pressure instrumentation. Connections were provided for sample taking and for liquid and air inlet and outlet. All feed tanks and product and waste receipt tanks were provided with sight glasses, liquid and air inlets and outlets, vacuum and sampler connections, and associated piping. Feed flow rates were controlled by calibrated displacement pumps.

B. Procedures

Each pilot-scale experimental run included two pulsed columns in series: (1) a center-fed extraction/scrub column with an aqueous feed; and (2) a stripping column into which the organic product from the top of the first column entered the bottom and was stripped of its uranium by the aqueous stream entering the top. The experiments were designed to obtain detailed aqueous and organic concentration profiles, fractional phase volumes, and the uranium inventory in each tested column. The operating conditions for the pilot-scale pulsed columns are shown in Table 1.

TABLE I
PILOT-SCALE PULSED-COLUMN OPERATING CONDITIONS (RUNS HS-1 THROUGH 3A-3)

Process	Column	Run ^b	Flow Rate (ml/min)				U Concentration (g/l)				HNO ₃ Concentration (M)				Dispersed Phase Holdup ^a (%)			Pulse	
			1AS	1AF	1AX	1BX	1AS	1AF	1AX	1BX	1AS	1AF	1AX	1BX	Extraction	Scrub	Stripping	Frequency (min ⁻¹)	Amplitude (cm)
Extraction/ Scrub	HS(1A)	HS-1	80	165	1050	--	0.0	273.3	0.0	--	2.97	2.44	0.0	--	15.3	14.1	--	83	2.0
		HS-2	80	145	1050	--	0.0	273.3	0.0	--	2.97	2.44	0.0	--	15.1	14.1	--	83	2.0
		HS-3	80	130	1050	--	0.0	273.3	0.0	--	2.97	2.44	0.0	--	15.0	14.1	--	83	2.0
		HS-4	150	285	1050	--	0.0	278.2	0.0	--	3.0	2.47	0.0	--	17.4	15.2	--	84	2.0
		HS-5	150	330	1050	--	0.0	278.2	0.0	--	3.0	2.47	0.0	--	17.9	15.1	--	84	2.0
		HS-6	150	350	1050	--	0.0	278.2	0.0	--	3.0	2.47	0.0	--	18.1	15.1	--	84	2.0
	2D(1A)	2D-1	145	310	1050	--	0.0	272.6	0.0	--	0.01	2.5	0.0	--	17.5	15.0	--	84	2.0
		2D-2	145	310	950	--	0.0	272.6	0.0	--	0.01	2.5	0.0	--	18.4	14.7	--	84	2.0
		2D-3	145	310	900	--	0.0	272.6	0.0	--	0.01	2.5	0.0	--	17.5	15.1	--	82	2.0
	2A(1A)	2A-1	104	650	280	--	0.0	25.3	0.0	--	1.0	3.0	0.0	--	26.3	19.8	--	82	2.0
		2A-2	104	650	200	--	0.0	25.3	0.0	--	1.0	3.0	0.0	--	27.2	20.6	--	82	2.0
		2A-3	104	650	240	--	0.0	25.3	0.0	--	1.0	3.0	0.0	--	26.8	20.2	--	82	2.0
	3A(1A)	3A-1	100	400	260	--	0.0	41.8	0.0	--	1.0	3.0	0.0	--	25.5	21.4	--	84	2.0
		3A-2	100	400	200	--	0.0	41.8	0.0	--	1.0	3.0	0.0	--	26.1	22.0	--	84	2.0
		3A-3	100	400	230	--	0.0	41.8	0.0	--	1.0	3.0	0.0	--	25.7	21.6	--	84	2.0
Stripping	1C(1BX)	HS-1	--	--	--	1300	--	--	--	0.0	--	--	--	0.0	--	--	(10.4)	57	2.0
		HS-2	--	--	--	1300	--	--	--	0.0	--	--	--	0.0	--	--	(10.1)	57	2.0
		HS-3	--	--	--	1300	--	--	--	0.0	--	--	--	0.0	--	--	(11.0)	57	2.0
		HS-4	--	--	--	1290	--	--	--	0.0	--	--	--	0.0	--	--	8.4	60	2.0
		HS-5	--	--	--	1300	--	--	--	0.0	--	--	--	0.0	--	--	(9.7)	60	2.0
		HS-6	--	--	--	1300	--	--	--	0.0	--	--	--	0.0	--	--	8.4	60	2.0
	2E(1BX)	2D-1	--	--	--	1130	--	--	--	0.0	--	--	--	0.0	--	--	8.8	60	2.0
		2D-2	--	--	--	1130	--	--	--	0.0	--	--	--	0.0	--	--	(9.8)	60	2.0
		2D-3	--	--	--	1130	--	--	--	0.0	--	--	--	0.0	--	--	(10.0)	60	2.0
	2B(1BX)	2A-1	--	--	--	240	--	--	--	0.0	--	--	--	0.3	--	--	15.1	72	2.0
		2A-2	--	--	--	240	--	--	--	0.0	--	--	--	0.3	--	--	(16.1)	72	2.0
		2A-3	--	--	--	240	--	--	--	0.0	--	--	--	0.3	--	--	(14.4)	71	2.0
	3B(1BS) ^c	3A-1	--	--	--	260	--	--	--	0.0	--	--	--	0.2	--	--	15.5	73	2.0
		3A-2	--	--	--	260	--	--	--	0.0	--	--	--	0.2	--	--	(16.7)	73	2.0
		3A-3	--	--	--	260	--	--	--	0.0	--	--	--	0.2	--	--	(16.3)	73	2.0

^aHoldup data in parentheses were determined experimentally; all other holdup data were calculated (see Sec. III.A.2).

^bRuns HS-1 through HS-3 were performed with 15 vol% TBP; all other runs used 30 vol% TBP. All runs operated at ~24°C.

^cData on the stripping stream (1BS) for this column are given under the 1BX heading.

The following is a brief description of the 15 pilot-scale tests that simulated the four cycles of the Purex process. The first three tests (HS-1 through HS-3) simulated the HS and 1C pulsed columns in the first uranium-plutonium cycle, and used 15 vol% TBP (tri-butyl phosphate) in n-dodecane as the organic phase. The other 12 tests, simulating the HS-1C, 2D-2E, 2A-2B, and 3A-3B pulsed columns, used 30 vol% TBP in n-dodecane. For tests HS-1 through HS-6, the HSF feed flow rate was varied as shown in Table I to determine its effect on column concentration profiles. For tests simulating the second uranium cycle (2D-2E columns) and the second (2A-2B columns) and third (3A-3B columns) plutonium cycles, the organic phase flow rate was varied as shown in Table I. For all tests, the 2-in.-diam 1A (dual process) pulsed column was used for extraction and scrubbing, and the 3-in.-diam 1BX column for stripping, with the

exception of the last three runs (3A-1 through 3A-3) where the 2-in.-diam 1BS stripping column was used.

During experimental runs, steadily operating positive displacement pumps were used for feeding each pulsed column with corresponding feed solutions. When the pulsed columns were at or near steady state, as determined by uranium assay of the outlet streams (column ends), samples of aqueous and organic phases were collected along each column and analyzed. The results of these analyses were used to develop the concentration profiles of uranium in the columns. Uranium concentrations were estimated by densimetric or titrimetric methods. The column uranium inventories for several runs were also estimated by analyzing the column dumps for the uranium in the partitioned aqueous and organic phases.

C. Concentration Profiles

Typical uranium concentration profiles for the extraction/scrub and stripping pulsed columns used in the pilot-scale experiments are shown in Figs. 2 and 3, respectively. For each column profile, both a single-phase, organic sample and a mixed-phase, aqueous and organic sample were withdrawn. Because of mixed-phase equilibrium following sample withdrawal, aqueous concentrations obtained from sample analyses were not equivalent to the concentrations at the time of sample withdrawal. Therefore, to estimate the actual concentrations of uranium at the time of sample withdrawal, a method proposed by Gier and Hougen¹¹ was employed.

The Gier and Hougen method is based on the following relationship between the volumes and concentrations of samples withdrawn from a pulsed column:

$$V(A)_t C(A)_t + V(O)_i C(O)_t = V(A)_i C(A)_i + V(O)_i C(O)_i$$

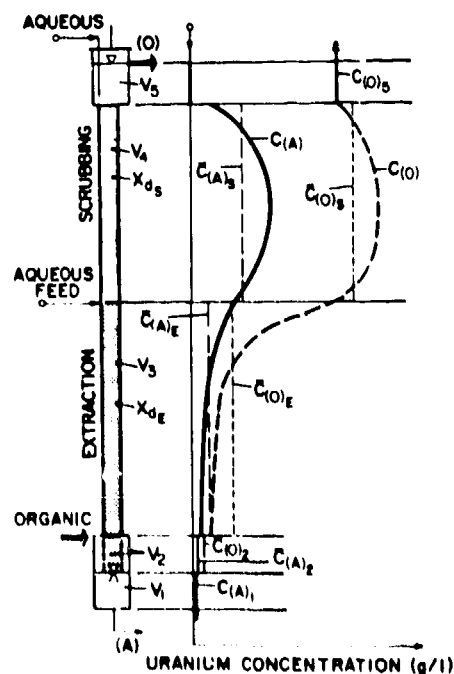


Fig. 2. Typical uranium concentration profile for an extraction/scrub pulsed column.

where $C(A)_t$ and $C(O)_t$ are, respectively, the true concentrations of aqueous and organic phases at the time of sample withdrawal, and $C(A)_i$ and $C(O)_i$ are, respectively, the observed (from analyses) concentrations of the two phases. $V(A)_i$ and $V(O)_i$ are, respectively, the volumes of the aqueous and organic fractions of the sample. From this relationship, $C(A)_t$, the actual concentration of uranium in the aqueous phase at the time of sampling can be estimated by measuring the other parameters of the above equation. This method was used to estimate the aqueous uranium concentration profiles corresponding to the organic profiles for each pilot-scale experimental run. The concentration profiles shown in Tables II and III for experimental runs 2A-3 and 2D-2, respectively, represent the type of data collected for each run.

III. PILOT- AND PLANT-SCALE COLUMN INVENTORIES

A. Inventory Estimation Methods

The uranium inventories in the pulsed columns of the pilot-scale experimental runs (Table

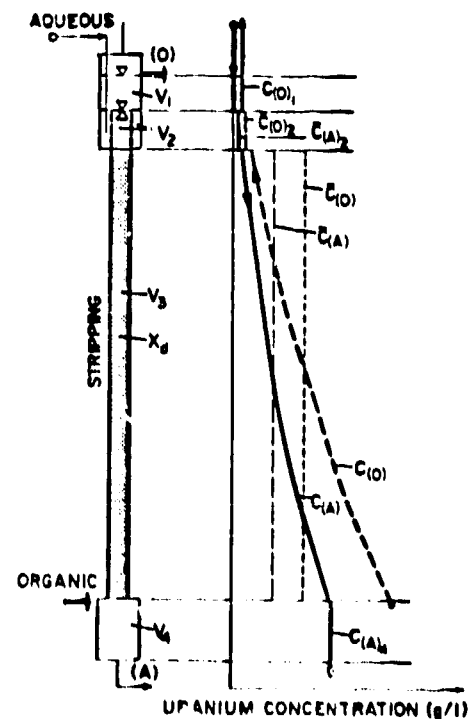


Fig. 3. Typical uranium concentration profile for a stripping pulsed column.

TABLE II
PILOT-SCALE CONCENTRATION PROFILE DATA

Experimental Run 2A-3

Extraction/Scrub Column (1A)				Stripping Column (1B)			
Sample ^a	Location ^b	Aqueous Uranium ^c	Organic Uranium ^c	Sample ^a	Location ^b	Aqueous Uranium ^c	Organic Uranium ^c
A-1	0.5	0.106	5.208	B-1	0.5	1.487	0.561
A-2	12.5	0.406	5.705	B-2	18.5	2.568	0.723
A-3	24.5	0.749	6.436	B-3	36.5	3.827	1.014
A-4	36.5	0.950	6.790	B-4	54.5	5.731	1.353
A-5	48.5	0.945	6.888	B-5	72.5	6.732	1.561
A-6	52.5	1.281	6.337	B-6	90.5	8.021	1.854
A-7	64.5	0.736	5.598	B-7	104.5	8.805	2.011
A-8	76.5	0.251	2.767				
A-9	88.5	0.110	0.840				
A-10	105.5	0.066	0.287				
A-11	129.5	0.047	0.045				

^aSee Fig. 1.

^bThe top of the working section corresponds to the value zero, and each stage has unit length.

^cThe values given are in units of g uranium/stage.

TABLE III
PILOT-SCALE CONCENTRATION PROFILE DATA

Experimental Run 2D-2

Extraction/Scrub Column (1A)				Stripping Column (1B)			
Sample ^a	Location ^b	Aqueous Uranium ^c	Organic Uranium ^c	Sample ^a	Location ^b	Aqueous Uranium ^c	Organic Uranium ^c
A-1	0.5	0.210	7.841	B-1	0.5	0.063	0.005
A-2	12.5	1.057	8.525	B-2	18.5	0.084	0.006
A-3	24.5	1.512	9.131	B-3	36.5	0.397	0.016
A-4	36.5	1.743	9.370	B-4	54.5	5.089	0.474
A-5	48.5	1.864	9.825	B-5	72.5	9.551	1.145
A-6	52.5	2.354	9.417	B-6	90.5	13.554	1.709
A-7	64.5	2.323	9.328	B-7	104.5	15.253	1.953
A-8	76.5	2.057	8.849				
A-9	88.5	1.002	6.213				
A-10	105.5	0.059	0.899				
A-11	129.5	0.008	0.059				

^aSee Fig. 1.

^bThe top of the working section corresponds to the value zero, and each stage has unit length.

^cThe values given are in units of g uranium/stage.

IV) and the plant-scale miniruns (Fig. 4 and Table V) were estimated both experimentally and predictively. The experimental inventory methods included (1) the volume-concentration measurement (or column dump) method used for both the pilot- and plant-scale runs and (2) the concentration profile--holdup measurement method used only for the pilot-scale runs. The first method (volume-concentration) is straightforward but provides no information about the effects of mass-transfer and hydrodynamic parameters on the inventory of an operating pulsed column.

1. Volume-Concentration Measurement.

The uranium inventories in the pilot-scale pulsed columns and in several plant-scale columns were estimated by performing volume and concentration measurements. Experimental uranium inventory data (column dumps) for the pilot- and plant-scale runs are summarized in Tables IV and V, respectively. After reaching (or attempting to reach in the case of the plant-scale and some pilot-scale columns) operational steady state, measurements were accomplished by shutting off all pulsed column inlet

TABLE IV
COMPARISON OF PREDICTED AND MEASURED
PILOT-SCALE PULSED-COLUMN INVENTORIES^a

Run	1A Pulsed Column (extraction & scrubbing)				1B & 1B5 Pulsed Columns (stripping)			
	Uranium Inventory (g)				Uranium Inventory (g)			
	Column Dump	Measured Concentration Profile and Holdup Data	Predictive Empirical Equation	Predictive Burkhardt Model ^b	Column Dump	Measured Concentration Profile and Holdup Data	Predictive Empirical Equation ^c	Predictive Burkhardt Model
HS-1	--	560	570	600	--	540	594	534
HS-2	--	490	497	510	--	450	490	415
HS-3	--	460	450	465	--	430	470	388
HS-4	--	1010	1012	1052	--	990	1030	995
HS-5	1140	1190 (+4%)	1144 (+0.4%)	1225 (+7%)	1190	1150 (-3%)	1206 (+1%)	1153 (-3%)
HS-6	--	1280	1223	1293	--	1210	1290	1201
2D-1	--	1140	1150	1140	--	1190	1305	1414
2D-2	1430	1510 (+6%)	1474 (+3%)	1609 ^c (+13%)	1315	1290	1310 (-0.4%)	1304 ^c (-0.8%)
2D-3	1610	1690 (+5%)	1650 (+2%)	1832 (+14%)	1330	1380 (+4%)	1300 (-2%)	1260 (-5%)
2A-1	--	730	722	701	--	1160	1180	1232
2A-2	1260	1310 (+4%)	1320 (+5%)	1405 (+12%)	940	870 (-7%)	940 (0%)	1130 (+20%)
2A-3	960	990 (+3%)	974 (+1%)	912 ^c (-3%)	1090	1050 (-4%)	1070 (-2%)	1184 ^c (+9%)
3A-1	830	860 (+4%)	865 (+4%)	836 (+1%)	--	970	855	993
3A-2	1320	1370 (+4%)	1344 (+2%)	1417 (+7%)	715	760 (+6%)	700 (-2%)	840 (+17%)
3A-3	1060	1130 (+7%)	1075 (+1%)	1063 (+0.3%)	820	880 (+7%)	775 (-5%)	934 (+14%)

^aParanthetical values are the inventory errors relative to the column dumps.

^bBased on "eyeball" fit of code-generated concentration profiles to observed data.

^cBased on least-squares fit of code-generated concentration profiles to observed data.

and outlet streams (at essentially the same time), draining and collecting the column contents individually in calibrated vessels, decanting the organic phase following phase separation, and assaying the uranium concentration in each liquid phase. The uranium inventory within a pulsed column was approximated by:

$$I = V(A) \cdot \bar{C}(A) + V(O) \cdot \bar{C}(O)$$

where

- I_T = total uranium inventory (g) in the column,
- $V(A)$ = total volume (l) of the aqueous phase in the column,
- $V(O)$ = total volume (l) of the organic phase in the column,
- $\bar{C}(A)$ = average uranium concentration (g/l) in the aqueous phase, and
- $\bar{C}(O)$ = average uranium concentration (g/l) in the organic phase.

The volume-concentration method is considered the most reliable but also the most disruptive inventory estimation method because it requires shutting off and draining the pulsed column(s) of interest. However, this method is useful for verifying pulsed-column inventories estimated by other methods.

2. Concentration Profile--Holdup Measurement. In this method concentration profiles were used in conjunction with the dispersed-phase holdup values given in Table I to estimate the pulsed-column uranium inventories for each pilot-scale experimental run. Again, the inventory results are shown in Table IV. Uranium concentration profiles for both the aqueous and organic phases were measured using several samplers located along each pulsed-column working section. The dispersed- and continuous-phase volume fractions, or holdups, for each pulsed column were estimated using the following equation derived⁹ from experimental phase-holdup data:

$$X_d \sim 0.185 (2fA_0 + \Delta U_{d-c})^{2.8}$$

where

- X_d = dispersed-phase holdup (2),
- f = pulse frequency (sec⁻¹),
- A_0 = pulse amplitude (cm), and
- $\Delta U_{d-c} = U_d - U_c$, that is, the difference between the dispersed- and continuous-phase, superficial linear velocities (cm/s).

This empirical equation describes the effects of pulse velocity (fA_0) and phase velocity difference (ΔU_{d-c}) on the dispersed-phase holdup (X_d).



For the dual-process 1A extraction/scrub pulsed column (Fig. 2) and the single-process 1BX and 1BS stripping pulsed columns (Fig. 3), the concentration-profile and dispersed-phase holdup data were used to estimate the uranium inventories as follows. For the stripping columns, for which the organic phase was dispersed in the aqueous phase,

$$I_T = V_1 \cdot C(O)_1$$

$$+ v_2 \cdot \{\bar{C}(A)_2 + x_d \cdot \left(\frac{D_w}{D_D}\right)^2 [\bar{C}(0)_2 - \bar{C}(A)_2]\}$$

$$+ v_1 \cdot (\bar{c}(\lambda) + x_1 \cdot (\bar{c}(0) - \bar{c}(\lambda)))$$

$$+ V_4 \cdot C(A)_4,$$

Dronium Inventory (kg)

^aParanthetical values are the total inventory errors relative to the column dumps.

^bBased on first-order perturbations about the expected (Burkhardt model) steady-state value.

^cBased on the column dump results for miniruns 1, 5, 6, and 7.

^dBased on the column dump results for mixtures 1, 5, and 7.

where

I_T = total uranium inventory (g) in the column.

V_1 to V_4 = volumes (l) of column sections (see Fig. 3),

$C(O)$ = uranium concentration (g/l) in the organic phase,

$\bar{C}(0)$ = average uranium concentration (g/l) in the organic phase of

C(A) = the column working section,
- uranium concentration (g/l) in
the aqueous phase,

$\bar{C}(A)$ = average uranium concentration (g/l) in the aqueous phase of the column working section,

X_d = dispersed-phase holdup,

D_w = diameter (cm) of the column working section, and

D_D = diameter (cm) of the column disengaging section.

Similarly, for the extraction/scrub pulsed column, for which the aqueous phase was dispersed in the organic phase,

$$I_T = V_1 \cdot C(A)_1$$

$$+ v_2 \cdot \{\bar{C}(O)_2 + x_{DE} \cdot \left(\frac{D_W}{D_n}\right)^2 [\bar{C}(A)_2 - \bar{C}(O)_2]\}$$

$$\begin{aligned}
& + V_3 \cdot \{\bar{C}(O)_E + X_{dE} \cdot [\bar{C}(A)_E - \bar{C}(O)_E]\} \\
& + V_4 \cdot \{\bar{C}(O)_S + X_{dS} \cdot [\bar{C}(A)_S - \bar{C}(O)_S]\} \\
& + V_5 \cdot C(O)_S,
\end{aligned}$$

where V_1 to V_5 are volumes (l) of column sections (see Fig. 2), and subscripts E and S designate the extraction and scrub column working sections, respectively.

Although the concentration profile--holdup measurement method is generally more complex and time-consuming than the volume-concentration method, it has the advantage of providing data for relating mass-transfer and hydrodynamic parameters to the inventory of an operating pulsed column. Such data, virtually nonexistent in the published literature, are essential for developing theoretical correlations relating in-process inventory to observable process parameters and for verifying contactor models.

The predictive inventory methods for both the pilot- and plant-scale runs included (3) development of empirical inventory estimators and (4) application of the Burkhardt¹² pulsed-column model. Predictive methods are useful for estimating the inventory in an operating pulsed column when insufficient data are available for estimating column profiles or, in the extreme, when no profile data are available.

3. Empirical Inventory Equations. An evaluation of the operating conditions and measured uranium inventories (Tables IV and V) for the pilot- and plant-scale runs resulted in the development of empirical equations for predicting the inventories in the pulsed columns tested.

For the pilot-scale runs, the empirical equations⁹ reflect the results that for the pulsed columns tested, the uranium inventory (Table IV) is proportional to the uranium feed rate into the column and inversely proportional to the stripping stream flow rate. The uranium feed rate is, in turn, a function of both the flow rate and concentration of the feed solution. The empirical equations for predicting the inventories in the pilot-scale stripping and extraction/scrub pulsed columns are shown below. The percent uncertainty listed with each equation below indicates the range of relative difference between the predicted and measured uranium inventories.

For the pilot-scale 1BX and 1BS stripping pulsed columns, which were operated to simulate the 1C, 2E, 2B, and 3B columns of the Purex process,

$$I_T \sim 0.45V_T \cdot \left(\frac{F_f}{F_{st}} \cdot C_f \right), \quad \pm 10\%$$

where

- I_T = total uranium inventory (g) in the column,
- V_T = total liquid volume (l) in the column,
- F_f = uranium feed flow rate (l/min),
- F_{st} = stripping (or extraction) flow rate (l/min), and
- C_f = uranium concentration (g/l) in the feed stream.

This equation applies over the range of

$$\left(\frac{F_f}{F_{st}} \cdot C_f \right) = 30 \text{ to } 100 \text{ g U/l}$$

and a stripping stream acidity of 0.0 to 0.3 M HNO_3 .

The following empirical equations were developed from the results of the pilot-scale 1A extraction/scrub pulsed column, which was operated to simulate the HS, 2D, 2A, and 3A columns of the Purex process. For the HS column,

$$I_T \sim 0.44V_T \cdot \left(\frac{F_f}{F_{st}} \cdot C_f \right), \quad \pm 4\%$$

This equation applies over the range of

$$\left(\frac{F_f}{F_{st}} \cdot C_f \right) = 30 \text{ to } 35 \text{ g U/l}$$

and a scrubbing stream acidity of ~ 3.0 M HNO_3 . For the 2D column,

$$I_T \sim 1.26V_T \cdot \left(\frac{F_f}{F_{st}} \cdot C_f - 50 \text{ g/l} \right), \quad \pm 4\%$$

This equation applies over the range of

$$\left(\frac{F_f}{F_{st}} \cdot C_f \right) = 75 \text{ to } 95 \text{ g U/l}$$

and a scrubbing stream acidity of 0.00 to 0.01 M HNO_3 . For the 2A and 3A columns,

$$I_T \sim 0.84V_T \cdot \left(\frac{F_f}{F_{st}} \cdot C_f - 30 \text{ g/l} \right), \pm 5\%$$

This equation applies over the range of

$$\left(\frac{F_f}{F_{st}} \cdot C_f \right) = 55 \text{ to } 85 \text{ g U/l}$$

and a scrubbing stream acidity of 1.0 M HNO₃.

The empirical equations shown above for predicting uranium inventories are specific to the tested pilot-scale pulsed columns. The functional form probably will be common to other columns, but the coefficient values in these equations are known to be affected by the physical dimensions of the particular pulsed columns investigated.^{9,13} For example, a preliminary analysis of the experimental operating and inventory data from the AGNS plant-scale miniruns (1, 5, 6, and 7) yielded the following empirical equations for predicting uranium inventories (Table V) in the 2A, 2B, 3A, and 3B pulsed columns. For the 2A (712-l total liquid volume) and the 3A (518-l total liquid volume) pulsed columns,

$$I_T \sim 0.72V_T \cdot \left(\frac{F_f}{F_{st}} \cdot C_f - 30 \text{ g/l} \right).$$

For the 2B column (425-l total liquid volume),

$$I_T \sim 0.39V_T \cdot \left(\frac{F_f}{F_{st}} \cdot C_f \right).$$

Finally, for the 3B column (468-l total liquid volume),

$$I_T \sim 0.38V_T \cdot \left(\frac{F_f}{F_{st}} \cdot C_f \right).$$

It can be seen in these equations that the coefficients for the plant-scale pulsed columns differ from those for the pilot-scale columns, mainly because of different column dimensions.

Theoretical derivations⁹ of the functional form of the empirical equations for both the pilot- and plant-scale pulsed columns predict the same effect of solute feed rate and stripping stream flow rate on the inventories. However, the validity and range of applicability of the plant-scale equations should be tested and verified (as were the pilot-scale equations) by performing additional plant miniruns under about the same operating conditions.

4. Burkhart Pulsed-Column Model. Several methods for simulating pulsed-column operation and estimating inventory were critically reviewed¹² by L. Burkhart. One of these, developed into a computer code by Burkhart and his coworkers, is considered here for illustration. In this code, a discrete-stage model is used, and solute concentration profiles are solved numerically via a Newton-Raphson procedure. Calculations are performed stagewise using finite difference equations that include reaction kinetics, empirical dispersed- and continuous-phase volume relationships, axial eddy-current diffusion (or backmixing), and non-equilibrium mass-transfer effects. The Burkhart model can be used to simulate either single-process (e.g., stripping) or dual-process (extraction/scrub) pulsed columns.

As implemented for the pilot-scale runs, the procedure for estimating column profiles using Burkhart's code resembles a general curve-fitting methodology. The mass-transfer and backmixing coefficients, unknown but required for input by the code, are treated as parameters to be estimated. Inventory estimates (Table IV) can be obtained by finding the code-generated column profile that agrees best (in a least squares sense) with the concentration profile approximated from measurements taken along the column. This optimization is performed by using the code in conjunction with a standard, derivative-free function minimization routine.

The estimated profile of the pilot-scale 2A-3 extraction/scrub column obtained using Burkhart's code is compared in Fig. 5 with the experimental data ("crosses" represent the organic data and "squares" the aqueous data). The corresponding estimated quantity of uranium is 932 g vs the dump value of 960 g (see Table IV).

The same procedures were applied to data obtained from the stripping column of the pilot-scale 2A-3 experiment, which are shown along with the estimated profiles in Fig. 6. The corresponding inventory estimate is 1184 g of uranium, as compared to a dump value of 1090 g (see Table IV).

Analysis of the pilot-scale 2D-2 experimental run followed along the same lines. Figures 7 and 8 display the predicted vs measured (Table III) uranium concentration profiles for the extraction/scrub and stripping columns, respectively. The inventory estimate corresponding to Fig. 7 is 1609 g, as compared to a dump value of 1430 g. And for Fig. 8, the corresponding inventory estimate is 1304 g vs a dump value of 1315 g (see Table IV).

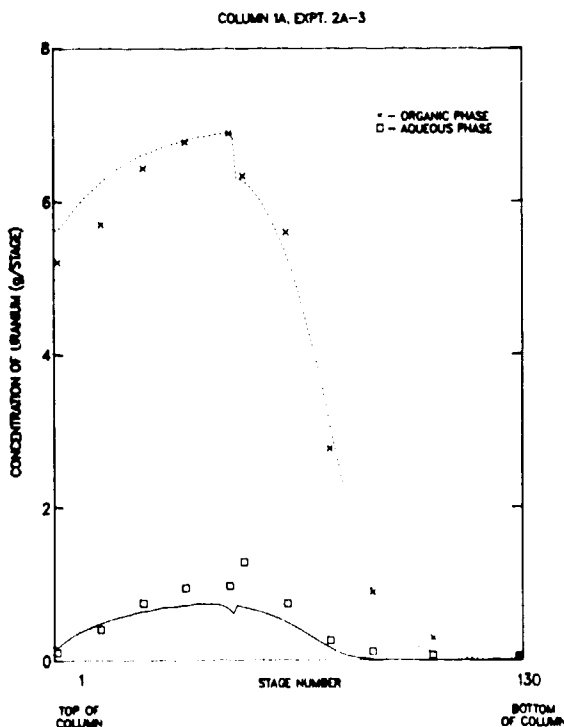


Fig. 5. Run 2A-3 extraction/scrub column profile--Burkhart model.

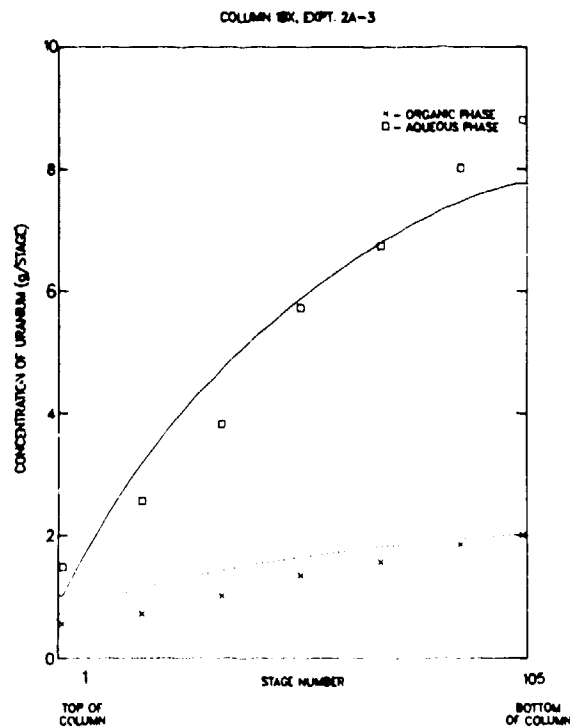


Fig. 6. Run 2A-3 stripping column profile--Burkhart model.

Alternatively, the concentration profiles, and hence the inventories, may be approximated by a smooth (for example, polynomial) function determined by the observed profile data, though this is not addressed in this paper. Such an approach would preclude the need for complex computer codes and detailed knowledge of column operation, but several profile measurements (six or more) probably would be required for good estimation.

For the plant-scale miniruns, for which no concentration profile measurements were taken, the predictive inventory estimators, labeled in Table V as (1) flow rate and concentration and (2) concentration, were used in conjunction with the Burkhart model to estimate the column inventories in near-real time. Values assumed for the mass-transfer and backmixing coefficients in the Burkhart model are the average values for the coefficients of the pilot-scale columns having the most similar flow-rate ratios, superficial linear velocities, and pulse velocities. The predictive inventory estimators approximated

the pulsed column inventories by a first-order Taylor series expansion about the steady-state inventories calculated using the Burkhart¹⁴ model for the expected run conditions. For the flow-rate and concentration-dependent estimator, the first-order terms depend on ratios of the measured concentrations, flow rate, and volumes. The concentration-dependent estimator is modified so that the first-order terms depend only on ratios of the measured concentrations and volumes.

In general, the estimates of the total uranium inventory for all four plant-scale pulsed columns are good to within 8% for the flow-rate and concentration-dependent estimator and to within 30% for the concentration-dependent estimator. However, inventory estimates for some individual columns have much larger relative errors, with the concentration-dependent estimator having a larger negative bias in both individual and combined inventory estimates. The actual run conditions may account largely

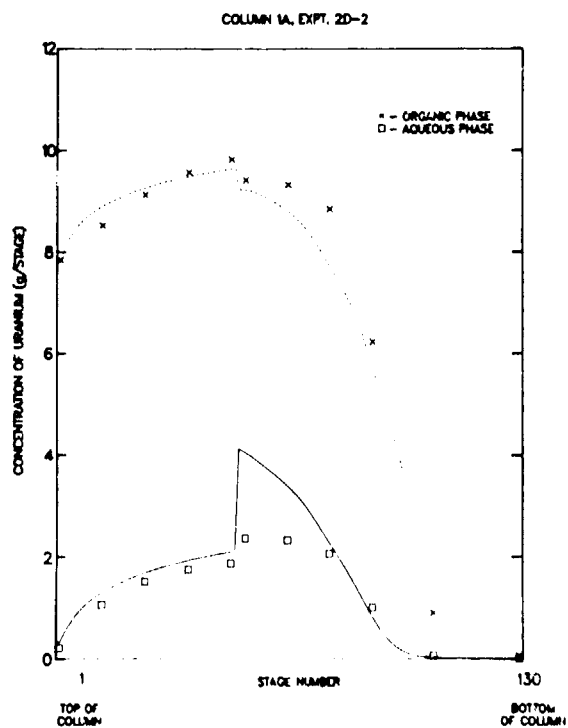


Fig. 7. Run 2D-2 extraction/scrub column profile--Burkhart model.

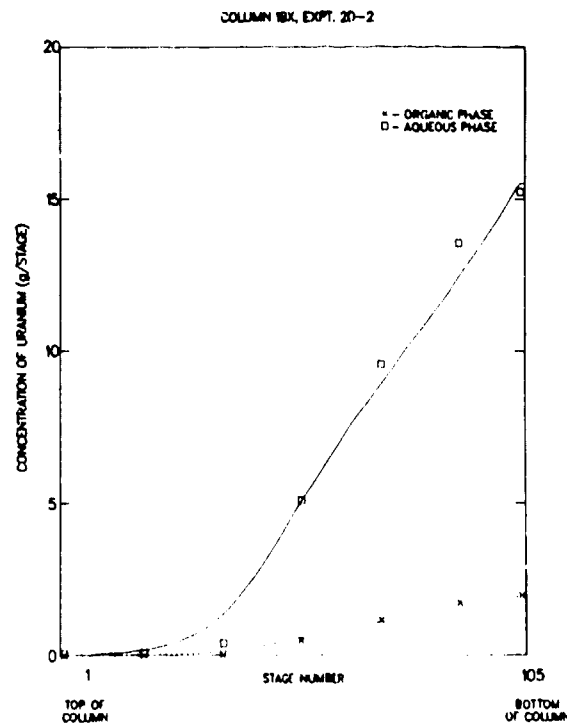


Fig. 8. Run 2D-2 stripping column profile--Burkhart model.

for the predicted vs measured inventory differences because (1) pre-dump run conditions often varied significantly from nominal conditions and (2) the current estimator models assume steady-state operations.

IV. SUMMARY AND CONCLUSIONS

Inventory estimation techniques for solvent-extraction contactors are being developed for near-real-time nuclear materials accounting and process control in fuels reprocessing plants. Extensive experimental tests were performed on AGNS' pilot- and plant-scale pulsed columns and comparisons were made of predicted and measured uranium concentration profiles and in-process inventories. Inventory estimation for the pilot-scale columns was demonstrated to 5-10% using both empirical equations coupled with input measurements and Burkhart model predictions coupled with input/output and column-profile measurements. Larger relative errors in the inventory estimates were observed for the plant-scale columns, primarily because (1) unlike the pilot-scale columns, these columns

operated with significant departures from steady state and (2) concentration profile measurements were not available for "calibrating" the Burkhart model to the specific column design and operating conditions.

Though the Burkhart model (see Sec. III) has been developed for estimating column profile and inventory based on operating conditions alone, unfortunately, operating conditions are never "known." Flow rates, feed concentrations, etc. are measured with error. More importantly, two key process parameters--the mass transfer coefficient and the backmixing coefficient--are usually unknown, but nevertheless required by this model. Hence, in the absence of column profile data for approximating these parameters, the accuracy of the inventory estimates generated by this model can be greatly limited as shown for the plant-scale pulsed column tests. Additional experimental and theoretical investigations are therefore necessary to develop this or another pulsed-column code to the point where it does not require the difficult task of measuring the column concentration profile.

Finally, similar studies should be performed to develop predictive methods for estimating plutonium inventories.

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